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A PROTECTIVE COATING SYSTEM FOR A TZM ALLOY RE-ENTRY VEHICLE

TECHNICAL REPORT

by

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A PROTECTIVE COATING SYSTEM FOR A TZM ALLOY RE-ENTRY VEHICLE

Technical Report AMRA TR 65-19

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A PROTECTIVE COATING SYSTEM FOR A TZM ALLOY RE-ENTRY VEHICLE

ABSTRACT

An electroplated coating system was developed to protect a TZM alloy re-entry vehicle from oxidation at high temperatures. The coating system, comprised of an undercoating of 0.0005 inch chromium, an intermediate coating of 0.001 inch nickel, and an outer coating of 0.0005 inch chromium, was adherent, oxidation resistant and thermal-shock resistant compatible with AMRAD TARGET Experiment requirements.

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INTRODUCTION

The Advanced Research Projects Agency (ARPA) is developing basic radar signatures to identify unknown objects, both metallic and nonmetallic, re-entering the earth's atmosphere. Each material shape produces a different ionization pattern which may be compared with a known set of parameters. Radar calibration for known re-entry shapes and materials may be accomplished by instrumenting the payload to provide correlated telemetry data which relate to radar profiles taken at specific points and speeds during re-entry. These data are essential for both the development of anti-missile radar systems and decoy re-entry bodies.

A metallic re-entry vehicle produces a wake with an ionization pattern upon re-entry that is representative of a large percentage of earth-bound foreign objects such as missile tankage, nose cones, or spacecraft structural members. The U. S. Army Missile Command was given the responsibility for the fabrication of such vehicles. For the metallic heat-sink type of re-entry vehicle, TZM molybdenum alloy (0.5 percent Ti, 0.08 percent Zr) was selected for the nose section, which is one of several scheduled for testing under the ARPA study. This selection was based on TZM's high strength-to-weight ratio at the temperatures which are encountered on re-entry (2700 F to over 3000 F). The ballistic coefficient value for the entire vehicle,

$$B = \frac{W}{C_D A},$$

where

W = weight of vehicle,

C_D = coefficient of drag,

A = radar cross section of vehicle,

is representative of specific types of objects re-entering the earth's atmosphere.

In addition to the high temperature - high strength requirements, the TZM alloy must be resistant to oxidation and ablation. Unfortunately, molybdenum and its alloys are susceptible to oxidation beginning at relatively low temperatures which becomes increasingly severe with increasing temperature. Gulbransen and Hickman¹ reported that below 750 F MoO₃ was the predominant oxidation product, but that above this temperature MoO₂ was the predominant species. They also found evidence of a complex oxide with the general formula Mo_xO_{3x-1}. Lustman² studied the oxides formed from 1100 to 1600 F and reported a yellow oxide at 1100 F and a crystalline, steel-gray oxide at the higher temperatures. At 1500 and 1600 F a molten oxide was identified which produces extremely rapid oxidation, since the liquid oxide can run off the surface and increased oxygen diffusion can occur through the liquid oxide phase. Jones et al.³ found that the scale formed on molybdenum consisted of two or three oxide layers. MoO₂ was the inner oxide layer and MoO₃ and Mo_xO_{3x-1} were the outer layers formed.

Molybdenum initially oxidized at a parabolic rate and then the rate became linear. This was attributed to the nonprotective nature of the outer MoO_3 layer, so that the rate of oxidation of the suboxide to the trioxide at the suboxide-trioxide interface is equal to the rate of diffusion of oxygen through the suboxide film to the metal-suboxide interface. It has been found that above 1500 F the MoO_3 vaporizes as quickly as it forms. This vaporization of oxide would contaminate the wake of the re-entry vehicle and interfere with the normal radar reflection pattern emanating from an otherwise smooth, continuous surface.

It was the objective of this study to develop a coating system which would protect the TZM molybdenum hemispherical nose section (Figure 1) from oxidation. This protection must be maintained for a minimum period of 16 seconds, during which the surface temperature rises from 80 to 3450 F as shown in Figure 2. This corresponds to a descent from an altitude of



Figure 1. RE-ENTRY VEHICLE
Hemisphere - Mo-TZM; Frustum and Fairing - Inconel X

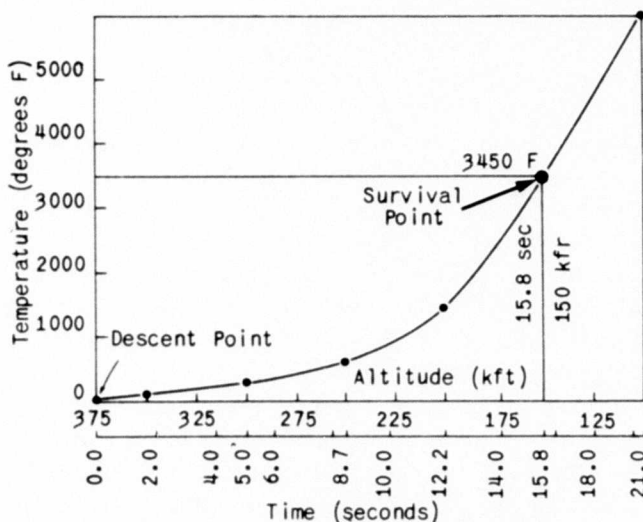


Figure 2. TRAJECTORY PARAMETER

375,000 to 150,000 feet. Below this altitude the temperature will exceed the melting point of the constituent metals of the vehicle and "burn-up" is anticipated. During the 16-second period, radar measurements must be made and conditions within the vehicle telemetered to receiving stations at the radar site. The information obtained must be computed and calibrated for identification analyses.

The coating materials selected must be resistant to high

temperature oxidation and retain adhesion to substrate under conditions of thermal shock. Any spallation of coating during re-entry will contaminate the wake. The thickness of coating is also a critical factor, since even minor changes in the weight or cross section of the vehicle would significantly affect its performance. The refractory oxides offer the best high-temperature oxidation protection. However, the ceramic-to-metal bond produced in most deposition processes leaves much to be desired. The behavior of nickel and chromium coatings in various combinations has been sufficiently promising to justify further investigation.

Although nickel plate provides a fair degree of protection it has not proved satisfactory because of relatively poor adherence to molybdenum, poor resistance to thermal cycling, rapid diffusion of molybdenum through nickel at 1800 to 2000 F, and the spalling characteristics of nickel oxide and nickel molybdate which are formed at high temperatures.⁴ However, nickel does have good resistance to attack by molybdenum trioxide and can bridge cracks or gaps in the underlying metal.

Molybdenum has a lower diffusion rate in chromium than in nickel and the solid solution Cr-Mo formed at the interface is more protective. The adhesion of chromium to molybdenum is better, even at high temperatures, since their coefficients of thermal expansion are similar. The combination of chromium and nickel is more promising; better yet is the chromium, nickel, chromium composite system where the addition of an outer layer of chromium is more effective. The superior performance of the combined chromium and nickel layers has been attributed to the protective nature of the spinel NiCr_2O_4 and Cr_2O_3 which are reportedly formed by the interaction of nickel and chromium and oxygen at high temperatures. In addition to chromium and nickel, the highly oxidation-resistant noble metals, platinum and rhodium, were selected for evaluation. Of the metals that can be deposited on molybdenum, chromium gives the best bond and therefore was selected as the initial deposit for all composite coating systems.

Of the many types of deposition processes, electrodeposition offers the advantages that it is a cold process and requires techniques and facilities which are generally available and fairly well established industrially.

Considering the factors of refractoriness, oxidation and thermal-shock resistance, adhesion, and ease and economy of application, the following electrodeposited composite coating systems were chosen for study and evaluated with respect to these properties:

- a. chromium, nickel, chromium;
- b. chromium, nickel, rhodium;
- c. chromium, nickel, platinum;
- d. chromium, nickel.

Because of limitations of weight, deposition efficiency, and reported oxidation data, the electroplate thicknesses selected were 0.0005 inch for chromium, 0.001 inch for nickel, and 0.0003 inch for platinum and rhodium.

ELECTROPLATING PROCEDURE

Methods to obtain adherent deposits on molybdenum have been reported in the literature. Couch et al.⁵ reported that good adhesion of chromium to molybdenum could be obtained fairly consistently by the use of Murakami's etching solution. Williams and Hammond⁶ reported another procedure for electrodepositing nickel and chromium on a 0.5 percent titanium molybdenum alloy.

Experiments were conducted using both of these procedures. However, with the TZM alloy it was difficult to obtain consistently good, adherent deposits. Satisfactory results were obtained finally by modifying the Williams and Hammond⁶ procedure to the following:

1. Alumina scrub.
2. Cathodic alkali clean (5% NaOH, 5% Na₂CO₃) 20 minutes, 50 amp/sq ft, 130 F.
3. Rinse at 130 F.
4. Anodic polish in 1:1 V/V H₂SO₄: H₃PO₄ for 3 minutes, 250 amp/sq ft, 130 F.
5. Rinse at 130 F.
6. Immerse in 50% NaOH for 10 seconds.
7. Rinse at 130 F.
8. Chromium plate (250 grams per liter CrO₃, 2.5 grams per liter H₂SO₄) at 200 amp/sq ft at 125 F.
9. Rinse at 130 F.
10. Nickel strike (Woods or chloride bath) for 10 minutes at 180 amp/sq ft, 110 F.
11. Rinse at 130 F.
12. Nickel plate (sulfamate bath), 50 amp/sq ft at 125 F.
13. Rinse at 100 F.
14. Anodic etch in H₂SO₄ for 5 minutes at 200 amp/sq ft room temperature.
15. Cathodic etch in H₂SO₄ for 30 seconds at 100 amp/sq ft, room temperature.
16. Rinse at room temperature.
17. Chromium plate for 60 minutes at 200 amp/sq ft, 125 F.
18. Warm rinse.

For the composite systems containing rhodium or platinum, these metals were electroplated after the nickel deposition, Step 12, using commercially available baths.

PREPARATION OF TEST SPECIMENS AND DETAILS OF TESTS

Cylindrical oxidation test specimens, 1/2 inch long by 1/2 inch in diameter, were machined from commercially available TZM molybdenum bar stock. These specimens were then electroplated with Cr, Ni; Cr, Ni, Cr; Cr, Ni, Pt; Cr, Ni, Rh, using the sequence of operations described previously. The plated specimens were examined visually for surface defects. Oxidation tests were conducted at temperatures of 2000, 2500, and 2700 F for a period of one-half hour on the plated specimens which were free of defects. The apparatus shown in Figure 3 permitted the automatic and continuous recording of weight loss or gain as a function of time, as the specimen

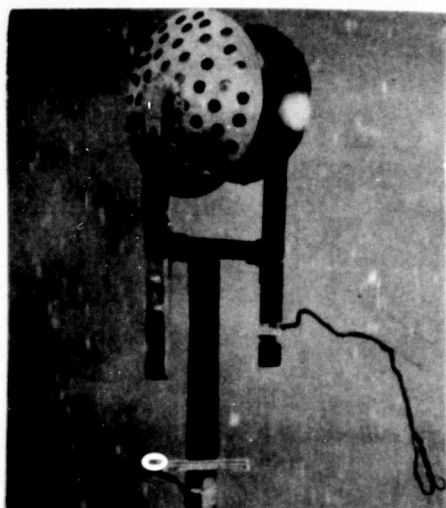


Figure 3. CONTINUOUS WEIGHING AND RECORDING OXIDATION APPARATUS

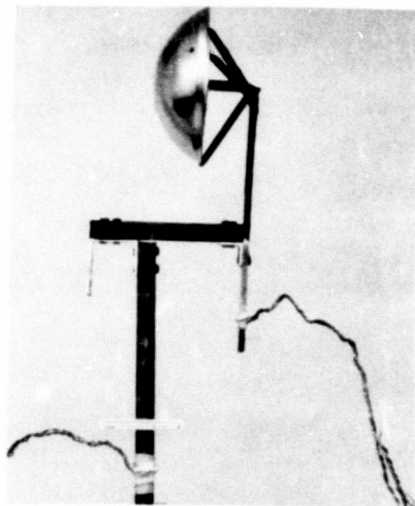
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underwent oxidation in quiescent air at 1 atmosphere. Using this technique, it was possible to follow the growth of protective films (weight gain) and any break in the protective layers with subsequent oxidation of the substrate TZM alloy (weight loss). The oxidation apparatus and technique has been described in Reference 7. After the oxidation runs, the specimens were visually examined, the oxidation products were analyzed by X-ray

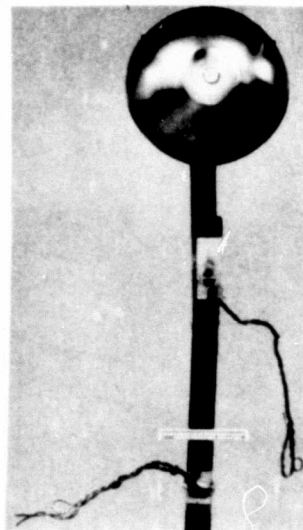
diffraction techniques, and the oxidation data (weight loss or gain versus time) were analyzed and evaluated. On the basis of this evaluation, two 1/4-scale TZM alloy nose cones (see Figure 4 for anode configuration, fixturing, and plated cone) were plated with the coating system that provided the best oxidation resistance. The first cone was visually examined



a. Anode Configuration



b. Fixturing



c. Plated Cone

Figure 4. TZM NOSE CONE WITH COMPOSITE CHROMIUM, NICKEL, CHROMIUM ELECTRODEPOSITS.

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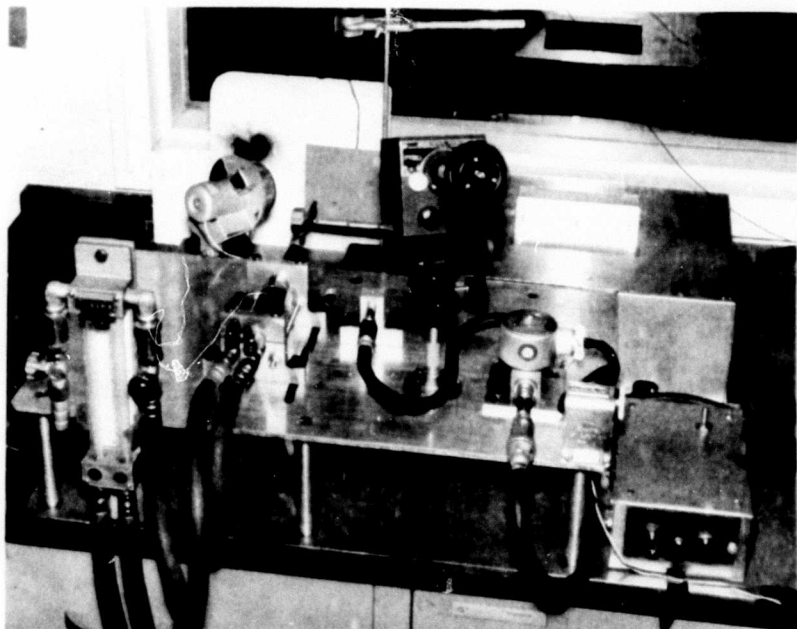


Figure 5. THERMAL SHOCK APPARATUS FOR REFRACTORY COATINGS

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for adequacy of plating procedure and appearance of electroplate. The second cone was subjected to thermal shock evaluation using the apparatus shown in Figure 5 and described in Reference 8. Briefly, the procedure consisted of impinging an oxyacetylene flame on one section of the plated cone for a period of one minute. Temperature measurements of the front and back surfaces were made with optical and radiation pyrometers sighted on the flamed zone and by a thermocouple welded to the rear of the surface of the cone on the flamed area. True front-surface temperatures in excess of 3000 F

were obtained within a 12- to 15-second time frame (note that the actual re-entry operating conditions indicate a temperature rise of 300 to 3500 F in approximately 12 seconds). After the heating cycle, the cone was cooled to 100 F by a one-minute blast of compressed air. Alternate cycles of heating and cooling were repeated until failure (spallation of coating and oxidation of TZM alloy) occurred.

RESULTS

Oxidation

Figure 6 is a plot of weight loss versus time for unprotected TZM alloy at a temperature of 2000 F. The alloy loss was approximately 150 milligrams per minute. At this rate, the specimen would be completely oxidized in a few hours. The weight loss was accompanied by the evolution of a white vapor indicative of volatilization of MoO_3 . An X-ray diffraction scan of the outermost surface of the oxidized specimen revealed the presence of both MoO_2 and MoO_3 . Thus, at 2000 F, MoO_2 and MoO_3 are formed and subsequently MoO_3 volatilizes as rapidly as it is formed.

The effect of Cr, Ni electroplates on the oxidation behavior of TZM alloy at temperatures of 2000 and 2500 F is shown in Figure 7a. At 2000 F the Cr, Ni layers completely protect the molybdenum for a period of 40 minutes, which is shown by the very slight weight gain observed. This weight gain is due to the formation of NiO which was identified by X-ray diffraction analysis at the outermost layer. At 2500 F there was an initial weight gain indicative of NiO formation, followed by a sudden weight loss due to the blistering and spallation of oxide and metal with subsequent oxidation of the TZM alloy and volatilization of MoO_3 . Oxidation of the TZM alloy occurred predominantly on the flat ends of the cylinder, indicating that the process of delamination was probably more advanced than local penetration around the circumference of the cylinder (see Specimen 2b of Figure 8). Breakdown or failure of the Cr, Ni plates occurred after one minute of exposure.

Figure 7b shows that a composite of Cr, Ni, Pt layers completely protects the TZM alloy from oxidation at 2000 F. An X-ray diffraction scan of the outer surface identified both NiO and Pt. It is evident that some Ni has diffused outward and subsequently oxidized. The slight weight gain noted in the curve is due to the NiO formation. The curve at 2500 F shows that, initially, a larger amount of oxide is formed due to the more rapid Ni diffusion rate at the higher temperature. There is a sudden loss in weight at one minute due to penetration of oxygen through breaks in the protective

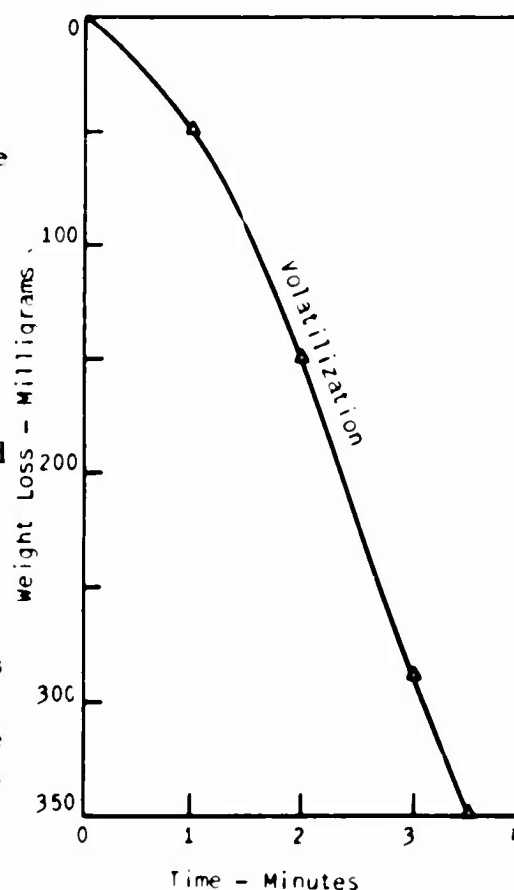


Figure 6. OXIDATION CURVE FOR TZM ALLOY AT 2000 F

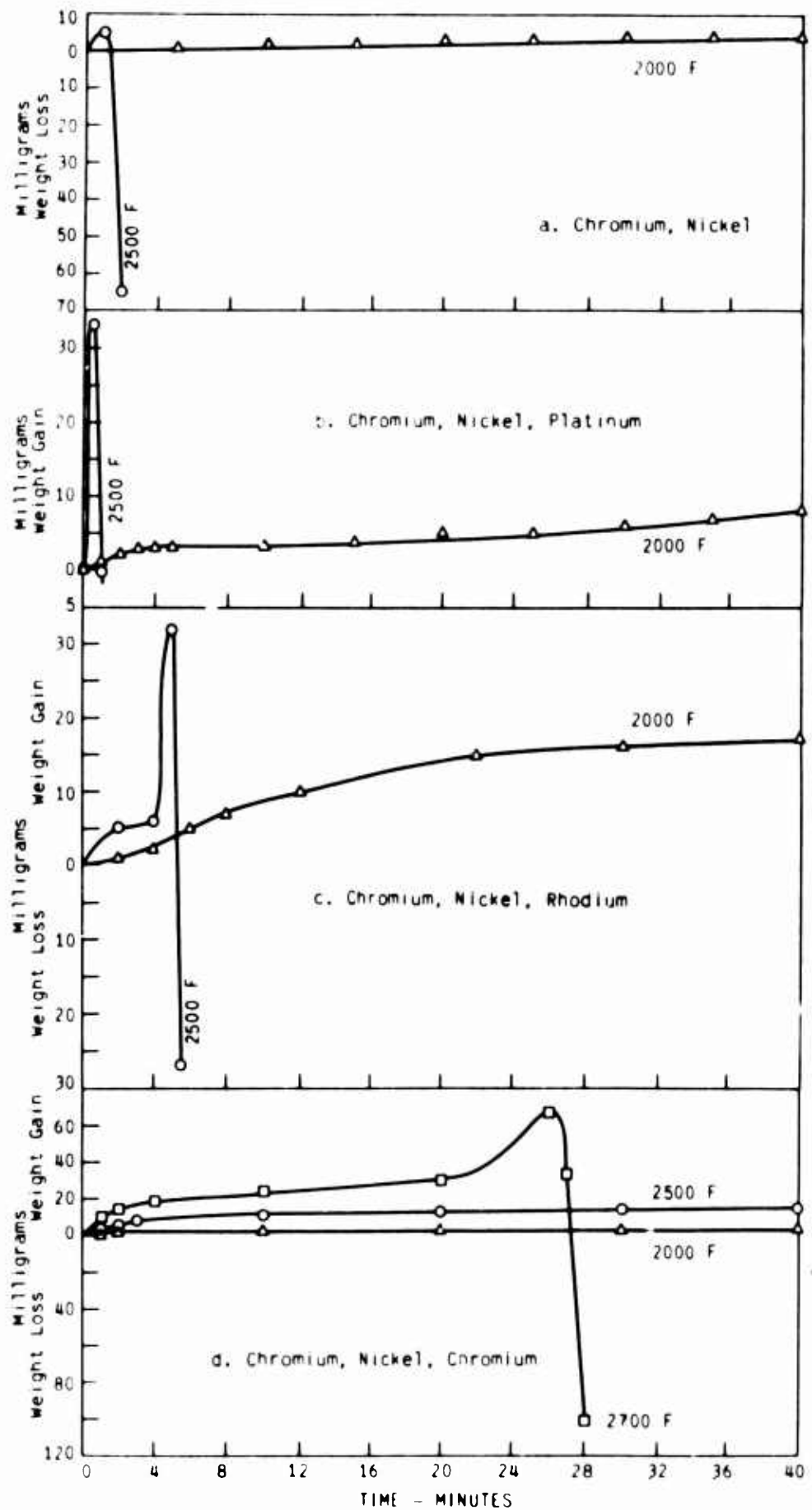


Figure 7. EFFECT OF TEMPERATURE ON THE OXIDATION OF TZM ALLOY WITH VARIOUS COATINGS

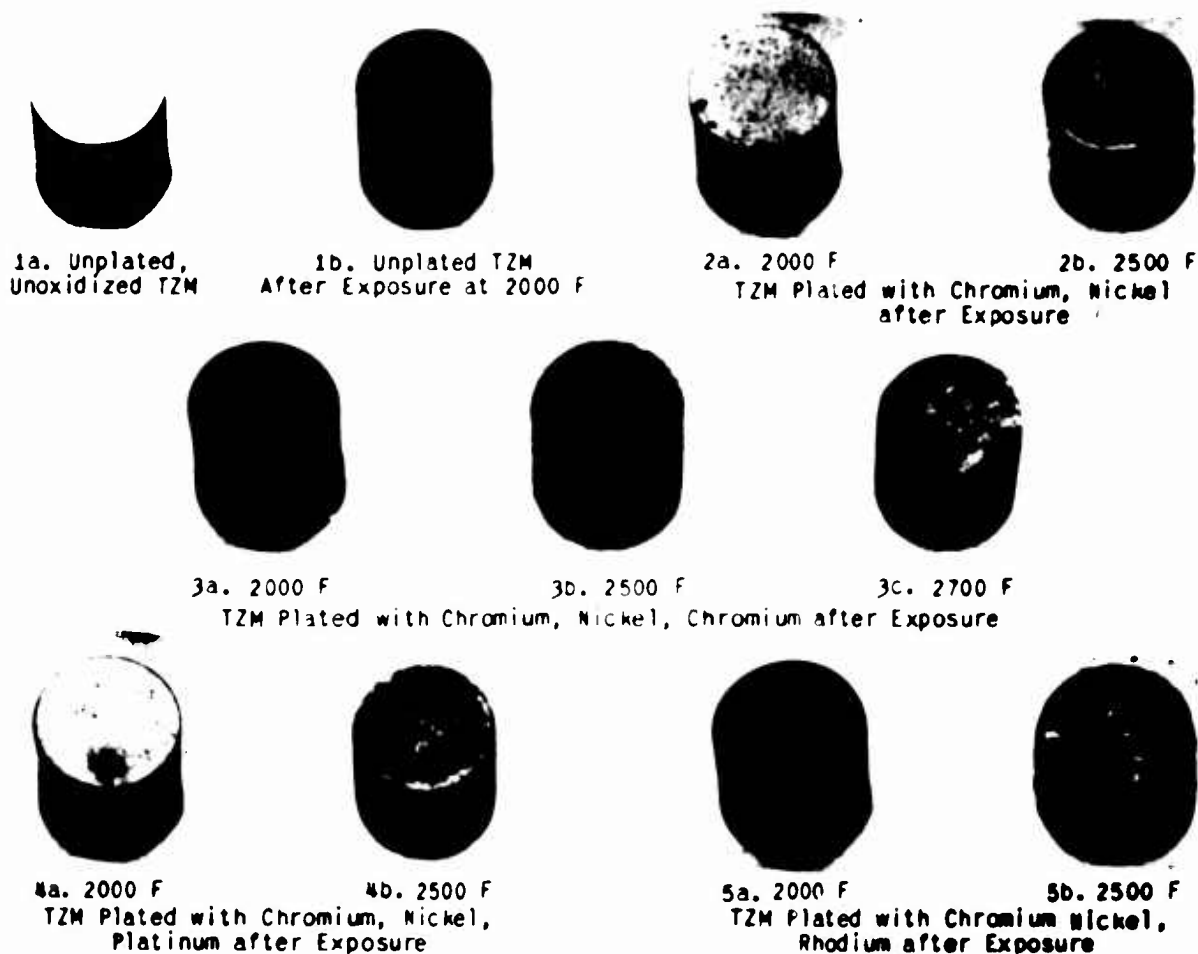


Figure 8. APPEARANCE OF UNPLATED AND PLATED TZM AFTER OXIDATION IN AIR

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layers and subsequent oxidation of the molybdenum alloy. Volatilization of MoO_3 was again observed at this point, indicative of failure at 2500 F. Similar results were obtained with the Cr, Ni, Rh system (Figure 7c); that is, the composite system protected the TZM alloy at 2000 F, while at 2500 F failure occurred within 4 minutes of exposure. Again, X-ray diffraction analysis showed that Ni diffused through the rhodium, subsequently oxidized to NiO, and the rate of diffusion increased with increasing temperature.

Figure 7d contains oxidation curves for the TZM alloy - Cr, Ni, Cr composite system at temperatures of 2000, 2500, and 2700 F. At both 2000 and 2500 F the Cr, Ni, Cr system completely protected the molybdenum alloy for a 40-minute period. The mechanism of protection appears to be the formation of Cr_2O_3 , which was the sole product in the outermost surface identified by X-ray diffraction analysis. No evidence of the formation of the protective spinel NiCr_2O_4 was found in any of the X-ray diffraction scans. At 2700 F, the protective nature of the Cr_2O_3 is reflected in the parabolic curve; the initial rapid gain in weight is due to the formation of the Cr_2O_3 which then prevents any further reaction or change in weight. This holds for the first 20 minutes of the oxidation run. After 20 minutes of exposure, there is a sudden gain in weight followed by a marked loss in weight or failure of the coating system. The large gain in weight prior to failure was also noted in the Cr, Ni, Pt and Cr, Ni, Rh systems at 2500 F. This may be attributed to the formation of solid oxides of MoO_2 and MoO_3 followed by volatilization, as shown by the weight loss.

The oxidation results may be summarized briefly by referring again to Figure 8 which is a photograph of the oxidized specimens. At 2000 F all coating systems were satisfactory (see Specimens 2a, 3a, 4a, 5a). Any discoloration of specimens was due to the formation of protective oxides. All coating systems except the Cr, Ni, Cr (Specimen 3b) exhibited failure at 2500 F. Specimens 2b, 4b, and 5b showed failure by blistering or spallation of coating and oxidation of the underlying molybdenum alloy. Although Specimen 3c (Cr, Ni, Cr) showed failure at 2700 F, this did not occur until 20 minutes had elapsed.

Thermal Shock

The oxidation runs demonstrated conclusively that the Cr, Ni, Cr system offered the TZM alloy the optimum protection at the highest temperature. Therefore, only the Cr, Ni, Cr composite coating applied to the TZM alloy subscale nose cone was subjected to thermal shock testing. This test showed that a true front-surface temperature in excess of 3000 F was obtained within 12 to 15 seconds of heating. Upon cooling with a blast of compressed air, the temperature was reduced to 100 F within one minute. Repeating alternate cycles of heating and cooling, the coatings-substrate system was able to withstand three complete cycles before any oxidation of the molybdenum alloy or vaporization of MoO_3 occurred. In addition, temperature measurements of the true front surface and the rear surface showed that the temperature of the underlying TZM alloy cone was several hundred degrees less than that on the surface of the coatings. This temperature difference demonstrates the thermal insulative capabilities of the coating system.

CONCLUSIONS AND RECOMMENDATIONS

The composite coating system consisting of layers of electroplated chromium (0.0005 inch thick), nickel (0.001 inch thick), chromium (0.0005 inch thick) performed satisfactorily under all test conditions including adhesion, oxidation resistance, and thermal shock resistance, and is recommended for use on the full-scale flight payload for AMRAD TARGET Experiments 2 and 4.

Oxidation tests indicated that this coating system provided adequate protection for the TZM alloy at 2700 F for a total of 20 minutes. Thermal shock tests demonstrated that the system could be exposed to re-entry conditions (heating from ambient temperature to greater than 3000 F in 12 to 15 seconds and cooling to 100 F in one minute) for 3 complete cycles before any deterioration was observed.

X-ray diffraction analyses indicate that the mechanism of protection is the formation of chromic oxide (Cr_2O_3) rather than the spinel NiCr_2O_4 . The chromic oxide is oxidation resistant at high temperatures (2000 to 2700 F) and is not subject to spallation at those temperatures.

All other coating systems evaluated were considered unacceptable due to failure at 2500 F during the oxidation tests.

The electroplating procedures developed for the Cr, Ni, Cr system on TZM alloy and used on the test cylinders and 1/4-inch-scale re-entry vehicle hemispheres were satisfactory. Some difficulties may be encountered when adapting these procedures to plating the full-scale vehicle. However, it is expected that this vehicle can be plated with the composite system satisfactorily.

ACKNOWLEDGMENT

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LITERATURE CITED

1. GULBRANSEN, E. A., and HICKMAN, J. W. *An Electron Diffraction Study of Oxide Films Formed on Mo, W and Alloys of Mo, W, and Ni.* Transactions, American Institute of Mining, Metallurgical, and Petroleum Engineers, v. 17, 1947, p. 371.
2. LUSTMAN, B. *Oxidation of Molybdenum in Air at 1100 - 1600 F.* Metal Progress, v. 57, 1950, p. 629.
3. JONES, E. S., MOSHER, J. F., SPEISER, R., and SPRETNAK, V. W. *The Oxidation of Molybdenum.* Corrosion, v. 14, 1958, p. 2t-8t.
4. HARWOOD, J. J. *Protecting Molybdenum at High Temperatures.* Materials and Methods, December 1956.
5. COUCH, D. E., SHAPIRO, H., TAYLOR, J. K., and BRENNER, A. *Protection of Molybdenum from Oxidation at Elevated Temperatures.* Journal of the Electro-Chemical Society, August 1958, p. 450-451.
6. WILLIAMS, C. and HAMMOND, R. A. *The Resistance to Oxidation of Nickel-Chromium Electrodeposits on Molybdenum.* Plating, January 1961, p. 58-59.
7. LEVY, M. *Oxidation of Pyrolytic Graphite Between 1250 F and 1850 F.* U. S. Army Materials Research Agency, WAL TR 851.41, May 1961; also Industrial and Engineering Chemistry, PR and D, v. 1, March 1962, p. 19-23.
8. LEVY, M. *Evaluation of Flame-Sprayed Coatings for Army Weapons Applications.* American Ceramic Society Bulletin, v. 42, no. 9, 7 September 1963.